Characteristics of pipe-scale in the pipes of an urban drinking water distribution system in eastern China

Jingqing Liu, Huanyu Chen, Qian Huang, Liping Lou, Baolan Hu, Sahle-Demessie Endalkachew, Nadagouda Mallikarjuna, Yonggui Shan and Xiaoyan Zhou

ABSTRACT

Pipes that carry drinking water have gradually aged. Events occurring with increasing frequency, such as substandard water quality in residential taps, red water, and black water, reveal the deterioration of the chemical stability of a drinking water distribution system (DWDS). Pipes in the DWDS serving City S, located in eastern China, were sampled to analyze the concentration and distribution of pollutants in pipe-scale of pipes of different materials, ages and diameters, and the factors (such as materials, age, and diameter) influencing the accumulation of pollutants were also investigated. The quantity of pipe-scale in the most commonly used gray cast iron pipe and ductile cast iron pipe (DN150) was 151.5–195.0 g·m^{-1} and 7.1–29.4 g·m^{-1}, respectively. The concentration of heavy metals in pipe-scale was positively correlated with the quantity of pipe-scale ($R^2 = 0.874$); the sequence of concentration of metals was Fe > Al > Mn, Zn > Pb, Cu > Cr, Cd. Galvanized steel pipe, with the highest degree of corrosion, had the highest concentration of heavy metals in pipe-scale. The morphology and composition of pipe-scale were substantially influenced by pipe material and age. For example, in the oldest galvanized steel pipe-scale, there was not only a large number of iron compounds but also some zinc composite oxides. In addition to hydrocarbons produced by microbial metabolism, there were microalgae metabolites and exogenous contaminants such as polycyclic aromatic hydrocarbons (PAHs). The concentrations of microbial metabolites increased with increasing service time.

Key words | contaminants, drinking water distribution system, heavy metal, organic pollutants, pipe-scale

Jingqing Liu
College of Engineering and Architecture,
Zhejiang University,
Hangzhou 310058,
China

Huanyu Chen
Qian Huang
Liping Lou (corresponding author)
Baolan Hu
College of Environmental and Resource Sciences,
Zhejiang University,
Hangzhou 310058,
China
E-mail: *loulp@zju.edu.cn*

Sahle-Demessie Endalkachew
Nadagouda Mallikarjuna
Yonggui Shan
Environmental Protection Agency,
Office of Research and Development, NRMRL,
Cincinnati, OH 45220,
USA

Xiaoyan Zhou
Shaoxing Water Environmental Science Institute Co. Ltd,
Shaoxing 312000,
China

Huanyu Chen
Binhai Industrial Technology Research Institute of Zhejiang University,
Tianjin 300020,
China

INTRODUCTION

The pipeline is one of most important parts of an urban drinking water distribution system (DWDS). Although many treatment plants keep improving water treatment processes to guarantee water quality, water at customers' taps is usually worse than that at the treatment plant owing to contamination during network transmission. In addition to serious pollution effects, such as 'red water' or 'colored water,' drinking water may contain high levels of turbidity, excessive amounts of iron and manganese, excessive bacteria, and other contaminants (Cerrato *et al.* 2006; Yang *et al.* 2012). In many cases, these are caused by the pipe-scale in the DWDS.

Drinking water from a treatment plant enters a DWDS with a physical load (particles), a chemical load (nutrients, heavy metal salts and organic matter) (Schock *et al.* 2008; Peng *et al.* 2010), and a microbial load (Liu *et al.* 2013), which gradually accelerate the formation of pipe-scale. Drinking water is usually delivered from the treatment

doi: 10.2166/ws.2015.183

plant to the client through tens or even hundreds of kilometres of pipeline. A series of complex reactions occur during this process, such as nitrification, corrosion (Regan *et al.* 2003; Renner 2008), and biofilm formation (Schwartz *et al.* 2003). In addition, trace heavy metal ions and organic matter in bulk water interact with pipe-scale and then gradually accumulate in the pipe, constantly changing the composition of the pipe-scale (Yu *et al.* 2010; Gonzalez *et al.* 2013) Thus, pollutants in pipe-scale are complicated and diverse, comprising a variety of metal oxides, salts and other inorganic matter, disinfection byproducts, microbial metabolites and other organic matter, as well as pipe biofilm.

Pipe-scale is widely present in all drinking water supply networks and may cause serious harm (Boulay & Edwards 2001; Edwards & Sprague 2001; Lytle *et al.* 2005; Calle *et al.* 2007; Copeland *et al.* 2007; Renner 2008; Kim & Herrera 2010; Xie & Giammar 2011; Benson *et al.* 2012; Świetlik *et al.* 2012; Gonzalez *et al.* 2013). A greater degree of corrosion can cause network damage and a reduction in the pipes' service life. When disturbed by events such as water quality changes, pipe breaks, and fire-fighting, pipe-scale can release metallic contaminants, reducing the quality of drinking water. Many metallic contaminants, including arsenic, lead, cadmium, mercury and uranium-based metals, are toxic to humans and other organisms (Domingo 1994; Valko *et al.* 2005; Beech *et al.* 2014). Any of these factors can cause water quality to fail to meet standards during water distribution.

Corrosion of pipes and growth of biofilm usually vary widely with differences in pipe material and age and bulk water properties, and the composition of pipe-scale also varies (Lee *et al.* 1980; Stanimirova *et al.* 2008; Ray *et al.* 2010; Pinto *et al.* 2012). In particular, the pipe material affects the composition of pipe-scale. Many studies have revealed that pipe material may dominate the composition of metallic compounds in pipe-scale. For example, the typical composition of iron corrosion products in cast iron pipes includes the oxy-hydroxides goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), magnetite (Fe_3O_4), hematite (Fe_2O_3), ferrous hydroxide ($Fe(OH)_2$), ferric hydroxide ($Fe(OH)_3$), and siderite ($FeCO_3$) (Sarin *et al.* 2004, Wang *et al.* 2012). In addition, quartz (SiO_2), calcite ($CaCO_3$) and other non-iron mineral components have frequently been detected (Peng *et al.* 2010). The most commonly detected copper compounds are cuprite (Cu_2O), tenorite (CuO), and malachite ($CuCO_3{\cdot}Cu(OH)_2$) (Merkel & Pehkonen 2006). These compounds store labile copper until it is released by a change in conditions (Calle *et al.* 2007). In PVC pipe, Cerrato found that manganese compounds accumulated substantially more than in cast iron pipes (Cerrato *et al.* 2006). Most of the lead compounds present in DWDSs are from a variety of sources, including lead pipes, tin-coated pipes, galvanized steel pipes, lead-soldered joints and fittings, brass materials, and cement-mortar lining. The corrosion products that normally form inside pipes are crosstie ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), plumbonacrite ($Pb_{10}(CO_3)_6(OH)_6O$), litharge (PbO), and plattnerite (PbO_2) (Lee *et al.* 1989; Kim & Herrera 2010). Galvanized steel pipe will usually accumulate zinc compounds (Gonzalez *et al.* 2013).

Organic pollutants not only affect the taste of drinking water but also accumulate in the pipe-scale, threatening water quality. Worse, in many cases they become nutrients for pipeline biofilms. Because of the limitations of trace analysis technology and methods of organic intermediates, there have been very few studies of organic pollutants in pipe-scale. Only a few preliminary reports on the types of organic pollutants have been published. These reports categorized organic pollutants into four sources: source water (Matilainen *et al.* 2010), pipe materials (Skjevrak *et al.* 2003; Durand & Dietrich 2005; Whelton & Nguyen 2013), metabolites of pipeline organisms (Skjevrak *et al.* 2004; Höckelmann & Jüttner 2005; Skjevrak *et al.* 2005; Beale *et al.* 2013) and disinfection by-products.

In contrast to developed countries, urban DWDSs in China did not come into wide service until the 1980s. At present in China, cast iron pipes account for 68% of these systems. Gray cast iron pipes, which are weakly resistant to corrosion, account for 51%; in some cities the figure is as high as 90%. Additionally, 85% of newly built pipelines still use metal pipes.

It was usually difficult to carry out systematic research of Chinese urban DWDSs, so much of the pipe-scale was collected from retired pipes, burst pipes, and simulation pipes (Yang *et al.* 2012). With the help of several social sectors of City S, located in eastern China, pipes in the DWDS serving the city were sampled to analyze the concentration and distribution of pollutants in the pipe-scale of pipes of different

materials, ages and diameters, and the factors influencing the accumulation of pollutants were also investigated.

MATERIALS AND METHODS

Sampling sites

At one time, the source water quality of the DWDS of City S was the highest in China. However, with increased development of the DWDS, the pipeline became complex and diverse (Figure 1). The water source was a natural river before 2002, when it switched to a reservoir. The flow velocity was low throughout the year. All the target pipes were serving the area without bends in the pipeline to ensure consistent hydraulic conditions. Additional information on the pipelines and water quality is given in Tables 1 and 2.

Sampling method

Twelve pipe samples were taken after 10:00 pm to avoid the influence of sunshine and high temperature. Pipe-scale was then collected, put into vials with Milli-Q water and refrigerated at 4 °C. All turbid liquid of pipe-scale was carefully metered in the laboratory. The liquid was centrifuged at 4,500 rpm for 10 minutes by a super-centrifuge (Thermo Sorvall RC+ centrifuge). The supernatant was collected and weighed using a sensitive balance (Mettler-Toledo AL204).

Analysis method

Analysis of metals

Turbid liquid of pipe-scale was put into Petri dishes, air-dried, and then ground to pass through a 100 mesh sieve. Approximately 0.2 g of air-dried scale was weighed using the sensitive

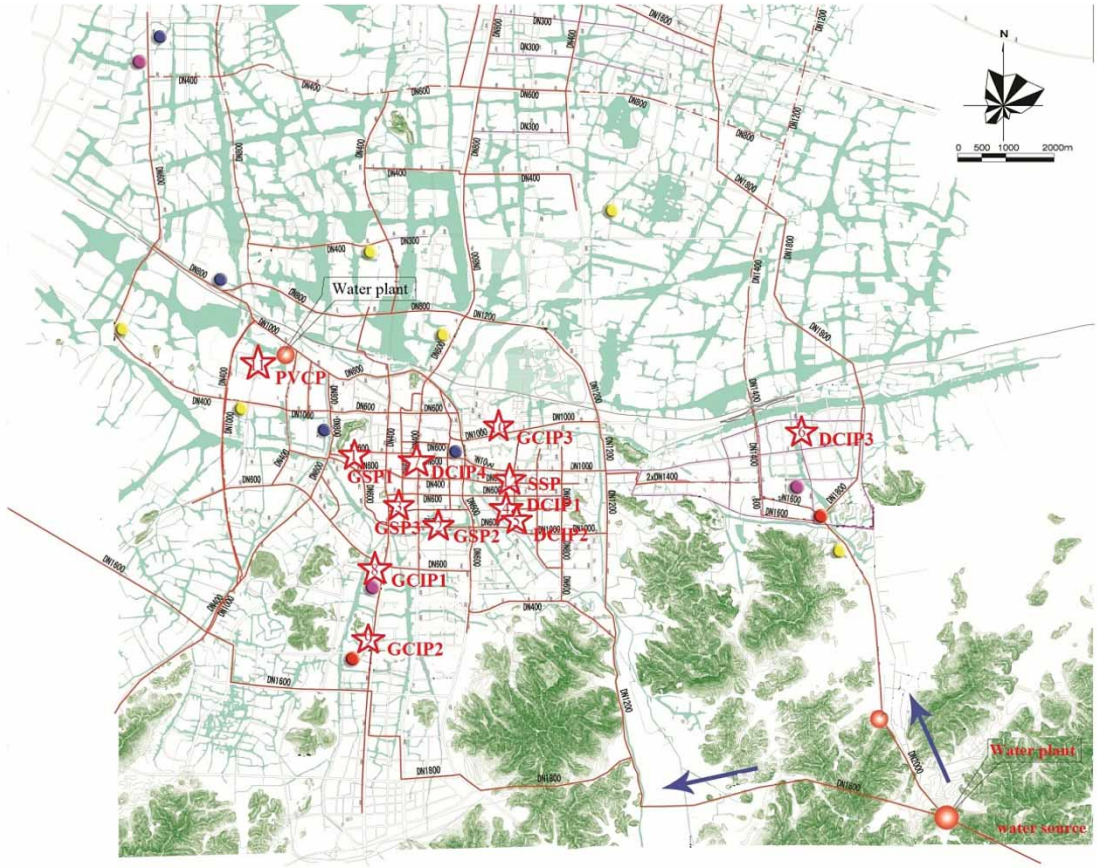

Figure 1 | The DWDS of City S.

Table 1 | Parameters of pipes

Sample ID	Pipe material	Pipe age (years)	Pipe diameter (mm)	Flow velocity ($m \cdot s^{-1}$)	Date	Quantity of pipe-scale ($g \cdot m^{-1}$)
GSP1	Galvanized steel pipe	12	DN80	<0.1	2013.09.29	16.0
GSP2		17	DN80	<0.1	2014.03.11	262.9
GSP3		23	DN80	<0.1	2013.04.03	47.8
DCIP1	Ductile cast iron pipe	6	DN150	<0.1	2013.10.15	28.0
DCIP2		6	DN150	<0.1	2014.03.13	7.1
DCIP3		9	DN150	<0.1	2014.03.18	8.0
DCIP4		11	DN150	<0.1	2013.09.25	29.4
GCIP1	Gray cast iron pipe	11	DN150	<0.1	2013.10.22	170.9
GCIP2		17	DN150	<0.1	2013.10.29	195.0
GCIP3		23	DN150	<0.1	2013.04.19	151.5
PVCP	PVC pipe	13	DN100	<0.1	2013.09.17	0.9
SSP	Stainless steel pipe	10	DN80	<0.1	2013.10.10	2.8

Table 2 | Water quality parameters of source water and treated water

Parameter	Source water	Treated water
pH	6.7–7.1	7.1–7.5
Turbidity (NTU)	0.94–2.77	<0.10
TDS (mg/L)	59–77	80–94
Alkalinity (mg $CaCO_3$/L)	14.0–22.4	22.1–28.5
Hardness (mg $CaCO_3$/L)	25.1–34.4	40.1–44.6
Total iron (mg/L)	0.024–0.056	<0.010
Cl^- (mg/L)	2.8–4.2	6.2–8.0
SO_4^{2-} (mg/L)	12.6–15.5	12.3–15.6
TOC (mg/L)	1.5–3.4	0.7–1.9
DO (mg/L)	5.6–12.2	6.9–10.1

TDS: total dissolved solids; TOC: total organic carbon; DO: dissolved oxygen.

balance (Mettler-Toledo AL204). Samples were acid-digested following a method (US EPA 3050B) based on microwave digestion (CEM MARS 5). An atomic absorption spectrometer was used for analysis (Thermo MKILM6) of metals, including Fe, Mn, Zn, Pb, Cu, Cr and Cd. Al content was determined via chrome azurol S complex formation (living standards for drinking water testing methods GB/T5750-2006) and UV-VIS spectrophotometry (UNICO UV-2100).

Analysis of organic pollutants

Wet pipe-scale samples were freeze-dried. The extraction steps for the freeze-dried solid samples were as follows. (1) Approximately 1 g of solid sample was placed in a 40-mL vial, then 5 g baked sodium sulfate and 30 mL methylene chloride (DCM) were added (2). The top of the vial was cleaned and sealed with a PTFE-sealed cap, shaken to test for leaks, and then carefully loaded in a shaker and shaken overnight at 150 rpm. (3) After being centrifuged at 1,200 rpm for 30 minutes, 1 mL liquid was removed for gas chromatography–mass spectrometry (GC-MS) analysis. (4) The concentrated solution was analyzed by the Agilent GC-MS. (5) The above four steps were repeated by using the mixed solvent acetone/hexane (1:1).

Semivolatile organic compound (SVOC) composition was analyzed using GC-MS (Agilent Technologies, Wilmington, DE, USA). Chromatography separations of samples were performed on an HP-5 ms fused silica capillary column (30 m × 250 μm i.d., 0.25 μm film thickness). The oven temperature was initially held at 40 °C for 1 min, then raised 15 °C min^{-1} to 120 °C and held for 1 min, followed by a second heating at 10 °C min^{-1} to 290 °C and held for 3 min. The helium gas flow rate of the column was 1.0 mL/min, and the temperature of the injector was maintained at 250 °C with a splitless mode and 1-μL injection volume of the samples. All analyses were performed in the SCAN mode of the MS, and the unknown organic contaminant was identified using the NIST 08 mass spectral library.

Figure 2 | Inner surfaces of various pipes before and after sampling.

Characterization of pipe-scale

The crystal structure of pipe-scale was analyzed using an X-ray diffractometer (XRD) (Bruker-P4). The operation parameters for XRD were as follows: Cu Kα radiation at 40 kV and 100 mA and a 2θ range from 5 to 90 °, with a 0.02 ° step and a 0.15-s count time at each step. Energy-dispersive spectrometer (EDS) analysis was conducted using a scanning electron microscope (JEM-5610LV).

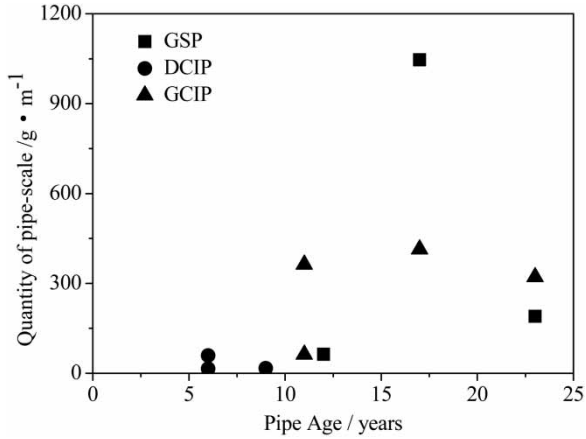

Figure 3 | Quantity of pipe-scale in pipes of different age and material.

RESULTS AND DISCUSSION

Total quantity of pipe-scale

The inner surface of the gray cast iron pipe (GCIP1-GCIP3) was more seriously corroded than that of other types of pipe, with a much larger tubercule (Figure 2). Therefore, the total amount of pipe-scale was higher: up to 195.0 g·m^{-1} (GCIP3) Figure 3. However, in the ductile cast iron pipe (DCIP1-DCIP4), there was almost no observable rust, and the inner protection liner was less corroded. Thus, the total amount of pipe-scale was smaller (7.1–29.4 g·m^{-1}). Not surprisingly, the likelihood of corrosion varied with the pipe material, and more pipe-scale accumulated in seriously corroded pipes. The result was similar in the other pipes.

In theory, the older the pipe was, the greater would be the probability of severe corrosion, resulting in a larger amount of pipe-scale. However, this was not the case. We found no clear correlation between content of pollutants in pipe-scale and pipe age. The differences may have resulted from the electrochemical corrosion of different pipes (Lytle *et al.* 2004).

Heavy metals

Table 3 shows that, regardless of the pipe material, the content of eight heavy metals in pipe-scale was in the following

Table 3 | Concentrations of heavy metals in pipe-scale per gram

Sample ID	Pipe age (years)	Pipe diameter	Fe (mg·g^{-1})	Zn (mg·g^{-1})	Mn (mg·g^{-1})	Pb (mg·g^{-1})	Cu (mg·g^{-1})	Cr (mg·g^{-1})	Cd (mg·g^{-1})	Al (mg·g^{-1})
GSP1	12	DN80	46.908	23.284	4.012	2.599	0.184	0.024	0.406	10.656
GSP2	17	DN80	690.858	2.613	4.355	0.524	0.097	0.354	<0.001	1.308
GSP3	23	DN80	109.347	0.561	1.993	0.073	0.027	0.027	<0.001	1.885
DCIP1	6	DN150	22.564	1.235	19.518	0.851	0.109	0.008	0.002	3.263
DCIP2	6	DN150	13.243	0.917	0.266	0.100	0.020	0.020	0.007	0.385
DCIP3	9	DN150	20.881	0.229	0.041	0.065	0.065	0.076	0.006	0.564
DCIP4	11	DN150	47.208	3.669	25.025	1.157	0.385	0.034	0.002	15.825
GCIP1	11	DN150	225.277	0.675	11.497	0.706	0.104	0.011	0.002	11.390
GCIP2	17	DN150	258.897	2.947	32.036	1.285	0.358	0.060	0.010	19.249
GCIP3	23	DN150	21.444	1.194	2.945	0.053	0.006	0.094	0.002	0.153
PVCP	13	DN100	5.159	1.873	0.671	0.141	0.035	0.035	0.035	0.106
SSP	10	DN80	23.395	6.561	2.935	0.168	0.203	0.097	0.009	1.874

order: Fe > Al > Mn, Zn > Pb, Cu > Cr, Cd. The concentration of Fe was the highest, ranging from 5.159 mg·g^{-1} to 690.858 mg·g^{-1}. This is because iron water supply pipes are the most common pipes in the DWDS (Gonzalez *et al.* 2013). In the gray cast iron pipe, which has more rust than the other types, the concentration of Fe in pipe-scale was much higher than that in the ductile cast iron pipe, which was another indication that the Fe in pipe-scale was mainly from corrosion (Lytle *et al.* 2005; Copeland *et al.* 2007). The 17-year-old DN80 galvanized steel pipe (GSP2) had by far the highest concentration of Fe in pipe-scale, reaching 690.858 mg·g^{-1}. This pipe was characterized by a long period of use, a very high degree of corrosion, and pipe tubercule that almost blocked the pipes. In addition to the PVCPs (5.159 mg·g^{-1}), several samples of ductile cast iron pipes had a low concentration of Fe. The common feature was the smooth lining material and a shorter period of use. The concentration of Fe in the SSP was only 23.395 mg·g^{-1}, owing to the greater corrosion resistance of its inner surface.

Because it is a common element in iron pipes (Lytle *et al.* 2004; Cerrato *et al.* 2006), the concentration of Mn was also relatively high. In pipes of different materials, the concentration of Mn in pipe-scale varied greatly. In the cast iron pipe-scale, the concentration of Mn was as much as 32.036 mg·g^{-1} (GCIP2), compared with only 0.671 mg·g^{-1} in the PVC pipe-scale (PVCP). The concentration of Mn was not as high as in a previous analysis of PVC pipes (Cerrato *et al.* 2006), indicating a trace amount of Mn in the source water of City S.

Flocculation of aluminum compounds in treated water would result in relatively high concentrations of Al in pipe-scale (Ona-Nguema *et al.* 2002, Huck & Gagnon 2004), especially in cast iron pipes. In the 17-year-old DN150 gray cast iron pipe (GCIP2), the Al concentration was up to 19.249 mg· g^{-1}.

In China, lead pipes and copper pipes have seldom been used; therefore, the concentrations of Pb and Cu in pipe-scale were very low. The concentration of Cr was less than 0.1 mg·g^{-1}in all samples except for GSP2.

Overall, the pipes with a high degree of corrosion and a long service time had more pipe-scale, and the concentrations of Fe, Al, Zn, Mn, Pb, and Cu in the pipe-scale were higher ($R^2 = 0.874$). This indicates that metal pollutants in pipe-scale are a reaction product of precipitation accumulation and corrosion of pipes.

Crystal structure of pipe-scale

Hydrotalcite-like compounds containing zinc aluminum and sodium aluminum, as well as aluminum phosphate ($AlPO_4$) and goethite (α-FeOOH), were observed in galvanized steel pipe-scale (Figure 4). The EDS data also showed the presence of Zn, which was consistent with the results shown in Table 3. As service time increases, a pipe's inner surface will form iron oxide (Sarin *et al.* 2004, Wang *et al.* 2012) and the inner liner

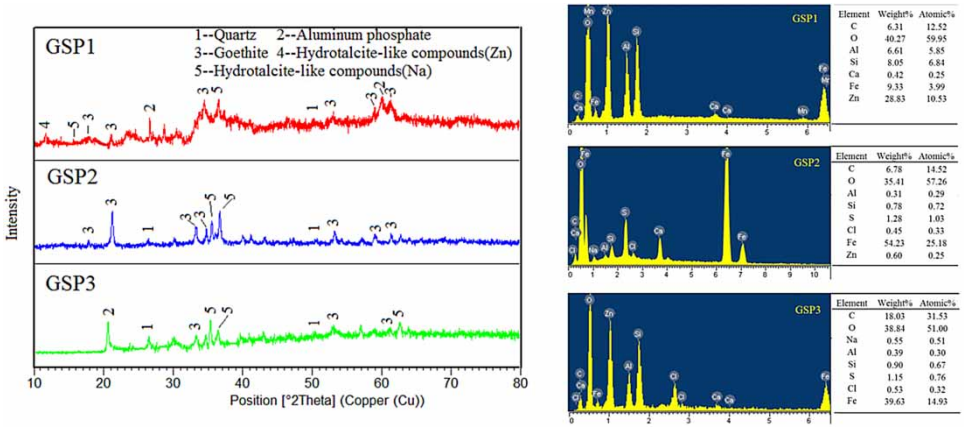

Figure 4 | X-ray diffraction patterns and energy-dispersive spectroscopy of pipe-scale from galvanized pipes.

may fall off. A pipe may then tend to form many iron oxides and metal composite oxides.

Pipe-scale from gray cast iron pipe that had not been long in service was composed mainly of quartz (SiO_2), goethite (α-FeOOH) and magnetite (Fe_3O_4) and other iron-containing metal compounds (Figure 5). Samples from older pipe had composite oxides containing calcium, iron, aluminum and magnesium, magnesium hydroxide and other composite silicon metal compounds.

There were more iron-containing metal compounds in gray cast iron pipe-scale than in ductile iron pipe-scale. The XRD patterns and EDS patterns (Figure 6) of ductile iron pipe-scale showed that differences in the components of the four samples were small, perhaps because of little difference in service life, an undamaged lining, and almost no rust. Only calcite ($CaCO_3$) and quartz (SiO_2) were observed in ductile cast iron pipe-scale.

In general, pipe material and age impacted the crystal structure of pipe-scale. Because of the undamaged lining and the similar pipe age, the differences in the composition of ductile cast iron pipe-scale were not significant. However, in galvanized pipes and gray cast iron pipes, the older the pipe was, the more complex was the composition of the pipe-scale. We conclude that, after a pipe has been in service

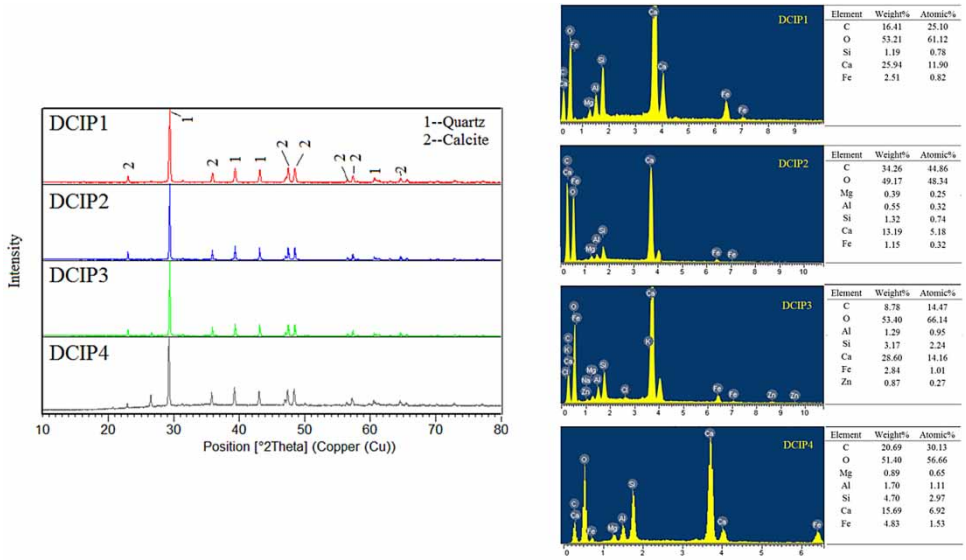

Figure 5 | X-ray diffraction patterns and energy-dispersive spectroscopy of pipe-scale from ductile cast iron pipes.

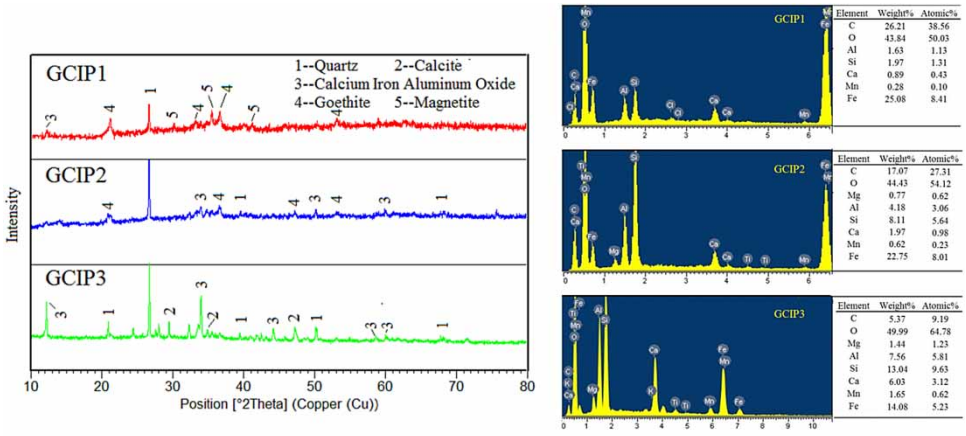

Figure 6 | X-ray diffraction patterns and energy-dispersive spectroscopy of pipe-scale from gray cast iron pipes.

for several years, the composition of its pipe-scale begins to change. With increasing service time, this difference becomes more pronounced.

Species of organic pollutants

Table 4 lists 40 types of organic pollutants in pipe-scale that were identified in our samples based on the best match with the MS library. A large number of organic pollutants that could not be identified are not included. In addition to some common types of hydrocarbons, such as octadecane, hexadecane, heptadecane and *n*-eicosane, which are formed by microbial metabolism, there were also some microalgae metabolites, such as oleamide (Bertin *et al.* 2012) and octadecenamide (Dembitsky *et al.* 2000). In addition, suspected exogenous polycyclic aromatic hydrocarbons (PAHs) (Peng *et al.* 2010), such as anthracene, phenanthrene, pyrene, and benzopyrene, were detected.

The organic pollutants accumulated in different pipe-scales varied substantially. The ages of the DCIP4, GCIP1, GSP1 and SSP were similar (approximately 11 years). The organic species in the DCIP4 and the GCIP1 were mainly hydrocarbons. Several amides and lipids were also detected. DCIP4 had the most abundant organic species, whereas GCIP1 had a higher content of amide, suggesting that more algae accumulated in the early service period, when the water source was a natural river. The two samples of galvanized steel pipe-scale were significantly different. Amides and lipids dominated in galvanized steel GSP1. Galvanized steel pipes are one of the most common peripheral pipes in the DWDS. As the last part of pipes into the client, the water was always in a low flow state, which was very conducive to the formation of pipe-scale and accumulation of pollutants. The organic species in the SSP were mainly PAHs, which was completely different from those in the cast iron pipe and galvanized steel pipe. This was due mainly to the smooth inner surface and less pipe-scale, which were not conducive to the accumulation of organic pollutants. Overall, the pipe material substantially impacted the organic pollution in pipe-scale. As a cumulative pollutant sinks, the more pipe-scale forms and the more microalgae metabolites accumulate.

The ages of ductile cast iron pipe samples DCIP1, DCIP2, DCIP3 and DCIP4 were 6, 6, 9 and 11 years, respectively. Fewer types of organic pollutants were detected in DCIP2, whose age was only 6 years, and they were mainly microalgae metabolites such as octadecenamide. A wide variety of organic hydrocarbons and PAHs were detected in the older pipe DCIP4 (11 years), suggesting that the initial pipes accumulated much more microalgae from the source water and accumulated relatively little biofilm. As service time increased, conditions became more conducive to pipeline biofilm growth. Thus, in the pipe-scale from older pipes, there were fewer types of microalgae metabolites and more types of microbial metabolites. The correlation between types of organic pollutants in the gray cast iron (GCIP1, GCIP2 and GCIP3) and galvanized steel (GSP1, GSP2 and GSP3) pipe-scale and pipe age was similar to that for the ductile cast iron pipe.

Table 4 | Organic pollutants in pipe-scale

	Chemical name	CAS no.	GSP1	GSP2	GSP3	DCIP1	DCIP2	DCIP3	DCIP4	GCIP1	GCIP2	GCIP3	SSP
1	1,2,3,4,5,6,7,8-Octathiocane	10544–50–0	–	–	–	–	–	–	√	√	√	√	–
2	1,2-Benzenedicarboxylic acid bis(2-ethylhexyl)ester	84-69-5	√	√	–	√	√	√	√	–	√	√	–
3	1,2-Benzenedicarboxylic acid, dibutyl ester	117-81-7	√	–	–	–	–	–	–	–	–	–	–
4	1.2:4,5-Dibenzpyrene	196-42-9	√	–	–	–	–	–	√	–	–	–	–
5	1-Hexadecene	000629-73-2	–	–	–	√	–	–	–	–	–	–	–
6	28-Nor-17beta(H)-hopane	036728-72-0	–	–	–	–	–	–	–	–	–	–	√
7	2-Chlorobenzyl bromide	611-17-6	–	–	–	–	–	–	–	–	–	–	√
8	2-Methylanthracene	613-12-7	–	√	√	–	–	–	–	–	–	–	–
9	7-Methylbenzo[b]phenanthrene	2541-69-7	–	–	√	–	–	–	–	–	–	–	–
10	9-Methylacridine	611-64-3	–	–	–	√	–	–	–	–	–	–	–
11	9-Octadecenamide	124-26-5	√	–	–	√	√	–	√	√	–	–	–
12	Anthracene	120-12-7	–	–	√	–	–	–	–	–	–	√	–
13	Benzenemethanol	100-51-6	√	–	–	–	–	–	–	√	–	–	–
14	Benzo(a)pyrene	50-32-8	–	–	√	–	–	–	–	–	√	√	–
15	Benzo[e]pyrene	192-97-2	–	–	–	–	–	–	–	–	–	–	√
16	Benzo[k]fluoranthene	207-08-9	–	√	–	–	–	–	–	–	–	√	√
17	Chrysene	218-01-9	–	–	√	–	–	–	–	–	–	–	–
18	Cyclopenta[cd]pyrene	27208-37-3	–	–	–	–	–	–	–	–	√	–	–
19	Docosane	629-97-0	–	–	–	–	–	√	√	–	–	–	–
20	Ethane, 2-chloro-1,1-diethoxy	621-62-5	√	–	–	–	–	√	–	–	–	√	–
21	Fluoranthene	206-44-0	–	–	–	√	–	–	√	√	√	√	√
22	Fluorene	86-73-7	–	–	√	–	–	–	–	–	–	√	–
23	Heptadecane	629-78-7	–	–	–	–	–	√	√	√	–	–	–
24	Hexadecanamide	629-54-9	√	–	–	√	√	–	√	–	–	–	–
25	Hexadecane	544-76-3	–	–	–	–	–	–	–	–	–	–	–
26	*n*-Dotriacontane	544-85-4	–	–	–	–	–	–	–	–	√	–	–
27	*n*-Eicosane	112-95-8	–	–	–	–	–	√	√	√	√	–	–
28	*n*-Heneicosane	629-94-7	–	–	–	–	–	–	√	–	–	–	–
29	*n*-Hexacosane	630-01-3	–	–	–	–	–	–	√	–	–	–	–
30	*n*-Nonadecane	629-92-5	–	–	–	–	–	√	√	√	√	–	–
31	*n*-Tricosane	638-67-5	–	–	–	–	–	–	√	–	–	–	–
32	Octadecanamide	124-26-5	√	–	–	√	–	–	√	√	–	–	–
33	Oleamide	301-02-0	–	–	–	–	√	–	√	–	√	–	–
34	Perylene	198-55-0	–	–	–	–	–	–	–	–	–	–	√
35	Phenanthrene	85-01-8	–	–	–	–	–	–	√	–	√	√	–
36	Pyrene	129-00-0	–	–	–	–	–	–	√	–	√	√	√
37	Stigmastane	601-58-1	–	–	–	–	–	–	–	–	–	–	√
38	Styrene	100-42-5	√	√	–	–	–	–	–	√	–	√	–
39	*n*-Tricosane	638-67-5	–	–	–	√	√	–	–	–	–	–	–
40	Triphenylene	217-59-4	–	–	√	–	–	–	–	–	–	√	√

In summary, the impact of pipe age on the type and content of organic pollutants in pipe-scale was greater than that of other factors. With an increase in service time, pipeline biofilms grow and exceed those of early microalgae from source water. As a result, the types of metabolites also change.

CONCLUSIONS

The following results were obtained.

1. When pipe ages and diameters were similar, the amounts of pipe-scale and pollutants in gray cast iron pipe were greater than those in ductile cast iron pipe; the amount of pollutants in galvanized pipe-scale was greater than that in PVCP and stainless pipe-scale. The morphology and composition of the pipe-scale from different types of pipes varied appreciably.
2. The concentration of heavy metals in pipe-scale was positively related to the quantity of pipe-scale ($R^2 = 0.874$). The sequence of metal concentrations was Fe > Al > Mn, Zn > Pb, Cu > Cr, Cd. The pipe material and the state of the inner surface lining clearly affected the type and content of heavy metal pollutants in pipe-scale. The concentrations of heavy metals in the pipe-scale of PVC pipe and stainless steel pipe were quite low because of their material properties and better corrosion resistance. The high concentrations of heavy metals in galvanized steel pipe-scale were due to severe corrosion and other reasons. The degree of corrosion in gray cast iron pipe and ductile iron pipe varied widely, so the concentration of heavy metals was different. The differences in the composition of different pipe-scales were also substantial. There were more types of iron-containing compounds in gray cast iron pipe-scale. However, in ductile cast iron pipe-scale, quartz and calcite dominated, and there were fewer iron-containing compounds because of the intact lining and less rust. More severely corroded galvanized steel pipe-scale had more iron-containing metal composite oxides, and some zinc-containing compounds were also detected.
3. In addition to hydrocarbons produced by microbial metabolism, there were microalgae metabolites and exogenous contaminants. The organic pollutants accumulated in different pipe-scales varied greatly, and the concentrations of microbial metabolites increased with increasing service time.

ACKNOWLEDGEMENTS

The authors thank the Key Special Program on the S&T Pollution Control and Treatment of Water Bodies (no. 2012ZX07403-003), the National Key Technology R&D Program (no. 2012BAJ25B07) and the National Natural Science Foundation of China (no. 51378455).

REFERENCES

Beale, D. J., Barratt, R. & Marlow, D. R. 2013 Application of metabolomics to understanding biofilms in water distribution systems: a pilot study. *Biofouling* **29** (3), 283–294.

Beech, I. B., Sztyler, M. & Gaylarde, C. C. 2014 Biofilms and biocorrosion. In: *Understanding Biocorrosion* (Liengen, T., Basseguy, R. & Feron, D., *et al.* (eds), pp. 33–56.

Benson, A. S., Dietrich, A. M. & Gallagher, D. L. 2012 Evaluation of iron release models for water distribution systems. *Critical Reviews in Environmental Science and Technology* **42** (1), 44–97.

Bertin, M. J., Zimba, P. V., Beauchesne, K. R., Huncik, K. M. & Moeller, P. D. 2012 Identification of toxic fatty acid amides isolated from the harmful alga *Prymnesium parvum* carter. *Harmful Algae* **20**, 111–116.

Boulay, N. & Edwards, M. 2001 Role of temperature, chlorine, and organic matter in copper corrosion by-product release in soft water. *Water Research* **35** (3), 683–690.

Calle, G. R., Vargas, I. T., Alsina, M. A., Pastén, P. A. & Pizarro, G. E. 2007 Enhanced copper release from pipes by alternating stagnation and flow events. *Environmental Science & Technology* **41** (21), 7430–7436.

Cerrato, J. M., Reyes, L. P., Alvarado, C. N. & Dietrich, A. M. 2006 Effect of PVC and iron materials on Mn(II) deposition in drinking water distribution systems. *Water Research* **40** (14), 2720–2726.

Copeland, R. C., Lytle, D. A. & Dionysiou, D. D. 2007 Desorption of arsenic from drinking water distribution system solids. *Environmental Monitoring and Assessment* **127** (1–3), 523–535.

Dembitsky, V. M., Shkrob, I. & Rozentsvet, O. A. 2000 Fatty acid amides from freshwater green alga *Rhizoclonium hieroglyphicum*. *Phytochemistry* **54** (8), 965–967.

Domingo, J. 1994 Metal-induced developmental toxicity in mammals: a review. *Journal of Toxicology and Environmental Health, Part A Current Issues* **42** (2), 123–141.

Durand, M. & Dietrich, A. 2005 Contributions of silane cross-linked PEX pipe to chemical/solvent odours in drinking water. *Off-Flavours in the Aquatic Environment VII* **55** (5), 153–160.

Edwards, M. & Sprague, N. 2001 Organic matter and copper corrosion by-product release: a mechanistic study. *Corrosion Science* **43** (1), 1–18.

Gonzalez, S., Lopez-Roldan, R. & Cortina, J.-L. 2013 Presence of metals in drinking water distribution networks due to pipe material leaching: a review. *Toxicological & Environmental Chemistry* **95** (6), 870–889.

Höckelmann, C. & Jüttner, F. 2005 Off-flavours in water: hydroxyketones and β-ionone derivatives as new odour compounds of freshwater cyanobacteria. *Flavour and Fragrance Journal* **20** (4), 387–394.

Huck, P. M. & Gagnon, G. A. 2004 Understanding the distribution system as a bioreactor: a framework for managing heterotrophic plate count levels. *International Journal of Food Microbiology* **92** (3), 347–353.

Kim, E. J. & Herrera, J. E. 2010 Characteristics of lead corrosion scales formed during drinking water distribution and their potential influence on the release of lead and other contaminants. *Environmental Science & Technology* **44** (16), 6054–6061.

Lee, S. H., O'Connor, J. T. & Banerji, S. K. 1980 Biologically mediated corrosion and its effects on water quality in distribution systems. *Journal of the American Water Works Association* **72** (11), 636–645.

Lee, R. G., Becker, W. C. & Collins, D. W. 1989 Lead at the tap: sources and control. *Journal American Water Works Association* **81** (7), 52–62.

Liu, G., Verberk, J. & Van Dijk, J. 2013 Bacteriology of drinking water distribution systems: an integral and multidimensional review. *Applied Microbiology and Biotechnology* **97** (21), 9265–9276.

Lytle, D. A., Magnuson, M. L. & Snoeyink, V. L. 2004 Effect of oxidants on the properties of Fe(III) particles and suspensions formed from the oxidation of Fe(II). *Journal American Water Works Association* **96** (8), 112–124.

Lytle, D., Sarin, P. & Snoeyink, V. 2005 The effect of chloride and orthophosphate on the release of iron from a cast iron pipe section. *Aqua* **54**, 267–281.

Matilainen, A., Vepsäläinen, M. & Sillanpää, M. 2010 Natural organic matter removal by coagulation during drinking water treatment: a review. *Advances in Colloid and Interface Science* **159** (2), 189–197.

Merkel, T. & Pehkonen, S. 2006 General corrosion of copper in domestic drinking water installations: scientific background and mechanistic understanding. *Corrosion Engineering, Science and Technology* **41** (1), 21–37.

Ona-Nguema, G., Abdelmoula, M., Jorand, F., Benali, O., Gehin, A., Block, J.-C. & Génin, J.-M. R. 2002 Iron (II, III) hydroxycarbonate green rust formation and stabilization from lepidocrocite bioreduction. *Environmental Science & Technology* **36** (1), 16–20.

Peng, C.-Y., Korshin, G. V., Valentine, R. L., Hill, A. S., Friedman, M. J. & Reiber, S. H. 2010 Characterization of elemental and structural composition of corrosion scales and deposits formed in drinking water distribution systems. *Water Research* **44** (15), 4570–4580.

Pinto, A. J., Xi, C. & Raskin, L. 2012 Bacterial community structure in the drinking water microbiome is governed by filtration processes. *Environmental Science & Technology* **46** (16), 8851–8859.

Ray, R. I., Lee, J. S., Little, B. J. & Gerke, T. 2010 The anatomy of tubercles: a corrosion study in a fresh water estuary. *Materials and Corrosion* **61** (12), 993–999.

Regan, J. M., Harrington, G. W., Baribeau, H., Leon, R. D. & Noguera, D. R. 2003 Diversity of nitrifying bacteria in full-scale chloraminated distribution systems. *Water Research* **37** (1), 197–205.

Renner, R. 2008 Pipe scales release hazardous metals into drinking water. *Environmental Science & Technology* **42** (12), 4241.

Sarin, P., Snoeyink, V., Lytle, D. & Kriven, W. 2004 Iron corrosion scales: model for scale growth, iron release, and colored water formation. *Journal of Environmental Engineering* **130** (4), 364–373.

Schock, M. R., Hyland, R. N. & Welch, M. M. 2008 Occurrence of contaminant accumulation in lead pipe scales from domestic drinking-water distribution systems. *Environmental Science & Technology* **42** (12), 4285–4291.

Schwartz, T., Hoffmann, S. & Obst, U. 2003 Formation of natural biofilms during chlorine dioxide and UV disinfection in a public drinking water distribution system. *Journal of Applied Microbiology* **95** (3), 591–601.

Skjevrak, I., Due, A., Gjerstad, K. O. & Herikstad, H. 2003 Volatile organic components migrating from plastic pipes (HDPE, PEX and PVC) into drinking water. *Water Research* **37** (8), 1912–1920.

Skjevrak, I., Lund, V., Ormerod, K., Due, A. & Herikstad, H. 2004 Biofilm in water pipelines; a potential source for off-flavours in the drinking water. *Water Science & Technology* **49** (9), 211–217.

Skjevrak, I., Lund, V., Ormerod, K. & Herikstad, H. 2005 Volatile organic compounds in natural biofilm in polyethylene pipes supplied with lake water and treated water from the distribution network. *Water Research* **39** (17), 4133–4141.

Stanimirova, I., Kubik, A. & Walczak, B. 2008 Discrimination of biofilm samples using pattern recognition techniques. *Anal Bio Chem.* **390**, 1273–1282.

Świetlik, J., Raczyk-Stanisławiak, U., Piszora, P. & Nawrocki, J. 2012 Corrosion in drinking water pipes: the importance of green rusts. *Water Research* **46** (1), 1–10.

Valko, M., Morris, H. & Cronin, M. 2005 Metals, toxicity and oxidative stress. *Current Medicinal Chemistry* **12** (10), 1161–1208.

Wang, H., Hu, C., Hu, X., Yang, M. & Qu, J. 2012 Effects of disinfectant and biofilm on the corrosion of cast iron pipes in a reclaimed water distribution system. *Water Research* **46** (4), 1070–1078.

Whelton, A. J. & Nguyen, T. 2013 Contaminant migration from polymeric pipes used in buried potable water distribution systems: a review. *Critical Reviews in Environmental Science and Technology* **43** (7), 679–751.

Xie, Y. & Giammar, D. E. 2011 Effects of flow and water chemistry on lead release rates from pipe scales. *Water Research* **45** (19), 6525–6534.

Yang, F., Shi, B., Gu, J., Wang, D. & Yang, M. 2012 Morphological and physicochemical characteristics of iron corrosion scales formed under different water source histories in a drinking water distribution system. *Water Research* **46** (16), 5423–5433.

Yu, J., Kim, D. & Lee, T. 2010 Microbial diversity in biofilms on water distribution pipes of different materials.

First received 26 August 2015; accepted in revised form 7 December 2015. Available online 22 December 2015